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CYCLE WITH LANTHANUM SULFITES AND SULFATES

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MODIFICATION OF THE SULFUR DIOXIDE-IODINE THERMOCHEMICAL
HYDROGEN CYCLE WITH LANTHANUM SULFITES AND SULFATES

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ABSTRACT

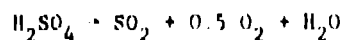
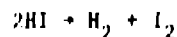
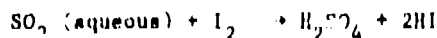
Variable composition, insoluble dilanthanum oxide-sulfite-sulfate-hydrates were prepared by reaction of lanthanum dioxymonosulfate with aqueous sulfur dioxide. These compositions reacted with iodine to yield sulfate in the solid phase, and hydrogen iodide and water in the gas phase. The highest yield of hydrogen iodide measured was 32% at 660 K for a few seconds reaction time of iodine with a reactant containing oxide-sulfite-sulfate with the approximate stoichiometry numbers, 0.9, 1.1, 1.0. Higher yields of hydrogen iodide were obtained by a second iodine oxidation after separation of the first solid product. These reactions are adaptable to a water splitting thermochemical cycle in which hydrogen is made by catalytic decomposition of hydrogen iodide at 700 K, and oxygen results from decomposition of the solid product at 1300 K.

KEYWORDS

Thermochemical hydrogen; water splitting, synthetic fuel; sulfur dioxide; iodine; hydrogen iodide; lanthanum dioxymonosulfate; dilanthanum oxide-sulfite-sulfate-hydrate; sulfur dioxide-iodine process.

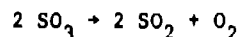
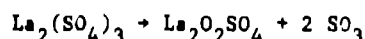
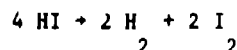
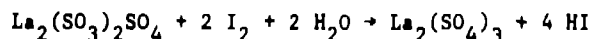
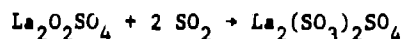
INTRODUCTION

The sulfur dioxide-iodine thermochemical process for water splitting has been demonstrated experimentally (Besenbruch and co-workers, 1980). It is identified as the GA Sulfur-Iodine Water-Splitting Cycle. This cycle has a high heat requirement for water management, but remains attractive for continued study because of the rapidity of the reactions:



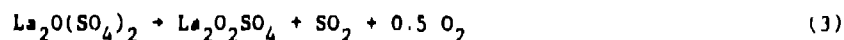
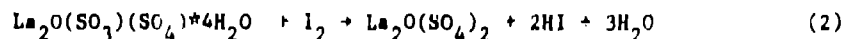
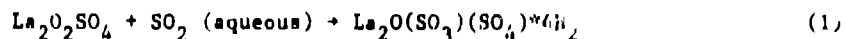
Several workers have tried modifications to the cycle for improving heat efficiency. Mason and Bowman (1982) showed improvement by using magnesium sulfite hexahydrate as the source of water for splitting, and using magnesium oxide as a recycle reagent. Sato and co-workers (1982) tested a nickel based cycle and claimed improved efficiency. Norman and co-workers (1982) tried an HBr extraction process on the GA Sulfur-Iodine cycle and found a small gain which was cancelled by other necessary steps.

Lanthanum dioxymonosulfate has been suggested as a recycle reagent for the sulfur dioxide-iodine process, in which all of the reactions are gas-solid or gaseous (Hollabaugh and Bowman, 1981):



They showed that lanthanum trisulfate decomposes rapidly at 1300 K to yield lanthanum dioxymonosulfate, sulfur trioxide, sulfur dioxide and oxygen (without a catalyst), but did not experiment with the other reactions in the cycle.

We report here on a cycle which utilizes lanthanum oxide-sulfite-sulfate-hydrate compositions with variable stoichiometry. The idealized cycle reactions are:



EXPERIMENTAL

The compositions which were reacted with iodine were made either at room temperature, 295 K, or at the boiling temperature of 365 K. A slurry of lanthanum dioxymonosulfate was stirred vigorously in a closed flask with sulfur dioxide and

lanthanum trisulfate concentrations both controlled. Reaction times were typically 30 min. Excess sulfur dioxide was removed by pumping. The crystalline precipitate which formed was easily separated by filtering, and it was air dried at room temperature after washing with water. Stoichiometric coefficients were determined by analyses for lanthanum, sulfite, sulfate, and water according to procedures developed earlier (Peterson, Foltyn, Onstott, 1980). Molecular weight was measured by weight loss at 1350 K, which yielded the dioxymonosulfate.

The hydrates were reacted with iodine in evacuated and sealed glass ampules of 20 ml size in a tube furnace. The gaseous products were separated by sealing in the capillary section of the ampule after cooling with powdered dry ice while heating the solid product at about 500 K. Hydrogen iodide was determined by titration to pH 7 with sodium hydroxide.

RESULTS

Experiments were done to find the effects of temperature, time of reaction, and compositions on yields of hydrogen iodide, and sulfite remaining in the solid product. Sulfite is consumed concurrently by iodine oxidation, and to a limited extent by sulfur dioxide evolution, and possibly by a parallel redox reaction in which sulfur is also evolved.

First experiments were done with $\text{La}_2(\text{SO}_3)_{2.25}(\text{SO}_4)_{0.75} \cdot 5.3 \text{ H}_2\text{O}$ by varying the reaction temperature and measuring hydrogen iodide yields. Largest yields were measured at 650 K. Further experiments were done between 600 and 700 K.

The effect of different compositions is shown by results in Table 1. A sulfite stoichiometry of 1.17 with sulfate equal to 0.95 gave the largest yield of hydrogen iodide. Unreacted oxide promoted higher yields as shown by the first four entries.

TABLE 1 Effect of Composition on Redox Yield of Hydrogen Iodide at 650 K

Dilanthanum stoichiometry				Reaction time, min	Iodine/sulfite starting ratio	HI yield percent
oxide	sulfite	sulfate	water			
1.30	0.80	0.50	3.8	135	2.77	13
1.05	1.04	0.91	4.4	120	2.08	23
0.88	1.17	0.95	4.5	125	1.84	27
0.50	1.55	0.95	5.8	135	1.32	15
0	2.25	0.75	5.3	180	2.49	10
0	2.32	0.68	4.9	135	1.11	10

Reaction times and temperature were varied for oxidation of the best composition in Table 1. Hydrogen iodide yields and sulfite remaining in the solid product are listed in Table 2. Short reaction times, which were determined by the procedure of removing the reaction vessel from the furnace, gave yields of hydrogen iodide comparable to long reaction times. This result indicates that the hydrogen iodide is formed by reaction of steam and iodine with the dehydrated starting material within a few seconds, or in shorter times. Activation may occur when hydrate water is evolved from the crystal.

Water added to the unreacted composition (Table 2) prior to oxidation at 650 K reduced the hydrogen iodide yield when the amount added was about half of the hydrate water. At room temperature, in the presence of iodine, the added water turned the composition a dark brown color. The loss in yield was a factor of 1.45.

TABLE 2 Effect of Reaction Time and Temperature on Redox Yield of Hydrogen Iodide by Oxidation of $\text{La}_2\text{O}_{0.88}(\text{SO}_3)_{1.17}(\text{SO}_4)_{0.95} \cdot 4.5 \text{H}_2\text{O}$ with Iodine

Reaction time, min	K	Iodine/sulfite starting ratio	Sulfite left after reaction*	HI yield percent
125	650	1.84	0.11	27
10	650	1.80	--	27
0.2	660	2.10	0.26	32
0.2	615	2.09	0.58	20
0.2	605	2.44	0.49	17
0.2	690	2.01	0.43	20
0.2	675	2.11	0.47	25
0.2, 0.2**	680	2.22, 2.32	0.15	20 + 22
20	650	0	1.06	0

*Stoichiometry number.

**Gaseous products separated before second reaction.

The yield of hydrogen iodide from the initial oxidation could be increased by adding water plus iodine to the separated solid product in a second reaction at the same temperature. Using this procedure doubled the yield when the added water was equal to the original hydrate water content. The next to last entry in Table 2 shows this result.

The last entry in Table 2 shows the effect of withholding iodine on sulfite loss, which was 10% in 20 minutes. Hydrate water was also lost. This loss of sulfite would not necessarily be the same with iodine present because of the possibility of iodine acting as a catalyst for sulfur dioxide and sulfur evolution. A careful thermogravimetric measurement of water loss and sulfur dioxide loss in the absence of iodine has not yet been done.

CONCLUSIONS

The water requirement for the sulfur dioxide-iodine thermochemical cycle can be minimized by employing an insoluble dilanthanum oxide-sulfite-sulfate-hydrate which reacts with iodine to yield sulfate and hydrogen iodide concurrently. A further increase in yield is obtained by separating the solid product and reacting it with iodine and an amount of water comparable to the original hydrate water. A separate hydrolysis step for hydrogen iodide formation is not required. The dilanthanum reactant composition can be tailored for optimum basicity and sulfite content.

ACKNOWLEDGEMENTS

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